

High near-infrared photoluminescence quantum efficiency from PbS nanocrystals in polymer films

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Abstract

We investigate the effect of film morphology and phase segregation in polymer/colloidal PbS nanocrystal films on the near-infrared photoluminescence quantum efficiency (PLQE) of the nanocrystals. A direct correlation between the size of closed packed nanocrystal phase separated domains and lower PLQE was established. Films with a near-infrared PLQE of up to 12% have been prepared.

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1. Introduction

Quantum dots confine excitons and therefore offer the size-tunable optoelectronic properties of artificial atoms. Colloidal nanocrystal (NC) quantum dots [1,2] offer the advantage of being solution-processible, and have been successfully used as the luminescent material in polymer-based light-emitting diodes (LED) in the visible [3] and infrared [4,5,6] range. As well, the size tunability of NCs permits spectral control of absorption for photovoltaic [7] and stimulated emission [8] applications.

In these devices, NCs are either embedded in a semiconducting polymer matrix or sandwiched between organic semiconductor layers. The semiconducting property of such host materials allows current flow, while their solution processibility provides the potential of low-cost processing and use in physically flexible systems. Although electroluminescence from NCs has been demonstrated in the near-infrared (NIR) range for fibre-optics applications [4,5,6], the efficiency of such devices remains low. Previous work [9] has

shown that energy transfer from the semiconducting polymer matrix to the luminescing NCs is not a limiting factor to the electroluminescence efficiency of these devices. Consequently, attention has been directed to maximizing the photoluminescence quantum efficiency (PLQE) of the NC itself. While PLQEs of greater than 50% have been reported for NIR-active NCs in solution [10], these values are dramatically reduced in films. Typical PLQE numbers reported for NCs emitting in the NIR region range from 0.5 to 1.5% in solid films at room temperature [5,11]. Because NCs are typically in an organic semiconducting film for optoelectronic applications and their PLQE is a limiting factor for electroluminescence efficiency, there is an urgent need to devise methods to increase the PLQE of NCs in such films.

Traditionally, dyes with known PLQE absorbing and luminescing in a similar spectral range to the NCs being investigated have been used as references for quantifying the PLQE of NC. While there are numerous efficient dyes spanning the visible spectral range, the few dyes in the NIR range are relatively inefficient. Comparing luminescence from efficient NCs with that from inefficient dyes can be difficult and often makes PLQE determination unreliable [5]. Using inappropriate dyes to quantify PLQE in the NIR range has led to considerable discrepancy in the numbers reported

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[5,10], making quantitative comparisons among them difficult.

In this work, we employ a technique involving an integrating sphere (IS) to obtain the absolute PLQE of NCs in NC–polymer composite films. We investigate the effect of different polymers and concentration ratios on the PLQE of the films. Electron microscopy is used to study the morphology of the films.

2. Experimental

The PbS NCs were synthesized as in [12]. The NCs have an average diameter of 5 nm. As synthesized, each NC is capped by a layer of organic ligand to prevent aggregation. In this work, the ligand is the oleate molecule which is an 18-carbon single chain terminated by a carboxylate group [9]. We employed four different polymers: MEH-PPV (poly[2-methoxy-5-(2'-ethylhexyloxy-*p*-phenylenevinylene)]), PMMA (poly(methyl methacrylate)), PF (poly[9,9-di-(2-ethylhexyl)-fluorenyl-2,7-diyl]), and PS (polystyrene). MEH-PPV and PF are semiconducting polymers while PMMA and PS are insulating polymers. All of these polymers were purchased commercially and are soluble in toluene. Composite solutions were made by mixing NC-in-toluene and polymer-in-toluene solutions of known concentrations.

For each polymer, a high-loading and a low-loading composite solution were made. The mass ratio of NC to MEH-PPV in the high-loading composite solution is 1:1 while that in the low-loading solution is 1:5. Since the four polymers used have different densities, mass ratios were adjusted for each polymer so that the volume ratios between NC and polymer in the composite solutions were kept constant. Each composite film was blade-cast from its composite solution on to a cleaned glass slide. The pure NC film was blade-cast from the NC-in-toluene solution. The optical densities of these films at the photoluminescence peak of the NCs were kept sufficiently low (≤ 0.02) that re-absorption of the photoluminescence is negligible during the PLQE measurement. The thicknesses of these films ranged from hundreds of nanometers to a few micrometers.

To obtain the absolute PLQE of the films in the NIR range, we built the experimental setup shown in Fig. 1. It is based on the design proposed in [13]. The sample is placed inside a spectralon-coated IS which has two ports. Excitation light from a laser at 831 nm enters into the IS through the input port. At the output port, a spectralon-coated baffle is placed to block direct irradiance from the sample. A liquid waveguide collects light from the output port of the IS and delivers it to a grating spectrometer which is coupled to a liquid-nitrogen-cooled Ge detector. The spectral response of the entire optical system is calibrated using a tungsten–halogen calibration lamp so that the true spectrum of the collected light can be recovered. The sample holder of the IS allows the sample to be illuminated either directly by the incoming laser beam (the

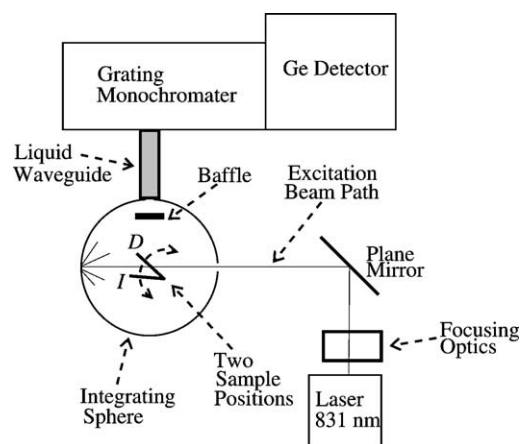


Fig. 1. The custom-built experimental setup for measuring the absolute PLQE of NCs in the near-infrared range. The two sample positions inside the integrating sphere are indicated by D and I.

D position), or indirectly by the scattered light inside the IS (the I position).

The PLQE of the NCs at the spot of the sample illuminated by the laser beam when the sample is in the D position is obtained from [13]:

$$\text{PLQE} = \frac{L_I P_D - L_D P_I}{L_E (L_I - L_D)}$$

where P_D and P_I are the areas under the NC photoluminescence spectra in the NIR range collected by the liquid waveguide when the sample is in the D and I position respectively; and L_I , L_D , and L_E are the areas under the excitation light spectra collected by the liquid waveguide when the sample is in the I position, in the D position, and absent from the IS, respectively. All of the spectra were taken at room temperature. Since none of the polymers used in this study absorbs at 831 nm from the excitation laser nor emits in the NIR range, the excitation absorbed and NIR luminescence emitted from the sample can be entirely attributed to the NC component of the film.

Transmission electron micrographs (TEM) were obtained using a Hitachi HD 2000 microscope operating at 200 kV. Diluted composite solutions were dropped onto TEM grids and the solvent evaporated. Images were taken in the dark-field mode, thus atoms with higher atomic numbers appear brighter. The presence of Pb atoms in the NCs provides very good contrast in this mode between the NC and polymer components.

3. Results and discussion

Typical NIR absorption and photoluminescence spectra of the films made are shown in Fig. 2. The NCs used had an excitonic peak at 1284 nm and photoluminescence peak at 1380 nm. For films luminescing in this range, there are major advantages to using the IS for measuring their absolute PLQE. First, no reference dye is required as both the

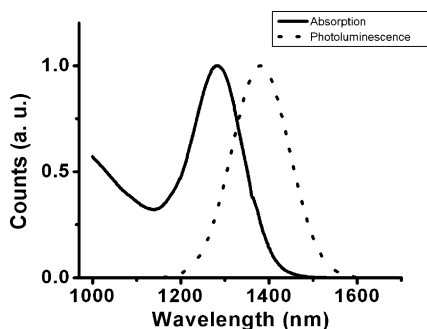


Fig. 2. Typical absorption and photoluminescence spectra of the NC-polymer composite films.

magnitudes and spectra of excitation absorption and NC luminescence are measured at the same spot on the sample. The lack of dyes having appropriate spectral characteristics and sufficient quantum efficiency becomes irrelevant in absolute PLQE measurement using the IS. Secondly, thickness uniformity of the sample is no longer a concern. This is especially important for film samples because the thickness of the film varies from spot to spot. Measuring the absorption and luminescence using separate instruments can cause significant error in PLQE measurement due to difficulties in consistent sample alignment, leaving the method susceptible to variances in film uniformity. Being able to measure both the absorption and luminescence at the same spot eliminates this concern. Thirdly, the incoming excitation light and the emitted luminescence scattered to any direction by the sample is captured by the inner wall of the spectralon-coated IS and collected by the waveguide equally. This is crucial for film samples since the surface of these NC-containing films can be sufficiently rough to cause significant scattering of the excitation light and luminescence. Prediction of the effect of this scattering process with mathematical models can be arbitrary and leads to significant error in PLQE measurement.

The PLQE of the pure NC film was measured to be $1.3 \pm 0.2\%$. This is similar to the 1% range reported for other NIR-active NCs in the literature [5,11]. The PLQE of the composite films are summarized in Fig. 3. The low-loading film of every polymer matrix used has a higher PLQE than the high-loading film. In the best case, the MEH-PPV low-

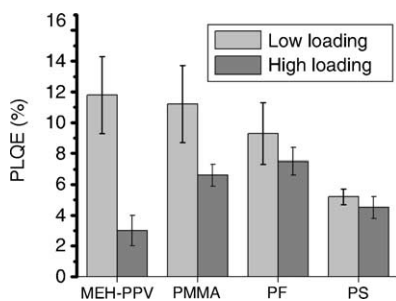


Fig. 3. PLQE of NCs in different polymer films with high and low relative NC content.

loading film reaches 12%, which is an eight-fold increase from the pure NC film. For PF, another semiconducting polymer, the low-loading film exceeds 9%. For the insulating polymers, the PMMA low-loading film reaches 11%, which is about the same as the low-loading films with semiconducting polymers. However, the PS low-loading film is only 5%, which is half the PLQE of the other low-loading films. As different polymers have different polarities, it is conceivable that the ligands of the NCs could have different affinities to different polymers—giving rise to different film morphologies.

TEM images shown in Fig. 4 reveal the morphology of the films. The PS high-loading film (Fig. 4a) has large interconnected domains of ordered close-packed NC networks. However, in the low-loading case for PS (Fig. 4b), the size of the ordered close-packed NC domains gets smaller and no network is observed. In the case of MEH-PPV, the NCs also form large ordered close-packed domains in the high-loading film (Fig. 4c). However, in the low-loading film (Fig. 4d), no ordered close-packed domains are observed. In the low-loading films of the other two polymers (PMMA and PF), the NCs do form ordered close-packed domains (Fig. 4e and f), although these are much smaller in size than for the respective high-loading films.

The observations from Figs. 3 and 4 imply that as the size of the ordered close-packed NC domains decreases, the PLQE of the NCs in these samples increases. This trend is consistent with the report [14] that PLQE of NCs in an insulating polymer matrix can be almost the same as that in solution if phase segregation of NCs from the polymer matrix can be prevented. When fewer NCs form domains, the distance between the NCs increases. This impedes energy transfer between them [11] and increases the PLQE, as it is less likely that energy is transferred to non-luminescing NCs. Moreover, the farther apart the NCs are, the less likely charge separation, a photoluminescence quenching mechanism, occurs between NCs [15]. In the extreme case of the MEH-PPV low-loading film where the NCs are not orderly close-packed, the PLQE of the NCs is the highest. It reaches 12%, which is at least an eight-fold increase from the typical 0.5 to 1.5% [5] reported for NCs luminescing in the NIR range.

Our results suggest that to achieve high PLQE from NCs in polymer films, one needs to choose the appropriate polymer and concentration ratios to disperse the NCs in the films. In NC-based optoelectronic applications, NCs are often embedded into semiconducting matrices for good electrical conductivity. Therefore, our NC-semiconducting polymer composite films can be readily used for the luminescing layer of electroluminescence devices. Furthermore, our process is simple and only involves mixing of the NC and polymer solutions. The films do not need further chemical processing such as polymerization and cross-linking [14]. Our results represent an improvement by almost an order of magnitude of the PLQE of NCs in semiconducting polymer films, which has been a limiting mechanism in increasing the efficiency of NC-based LEDs.

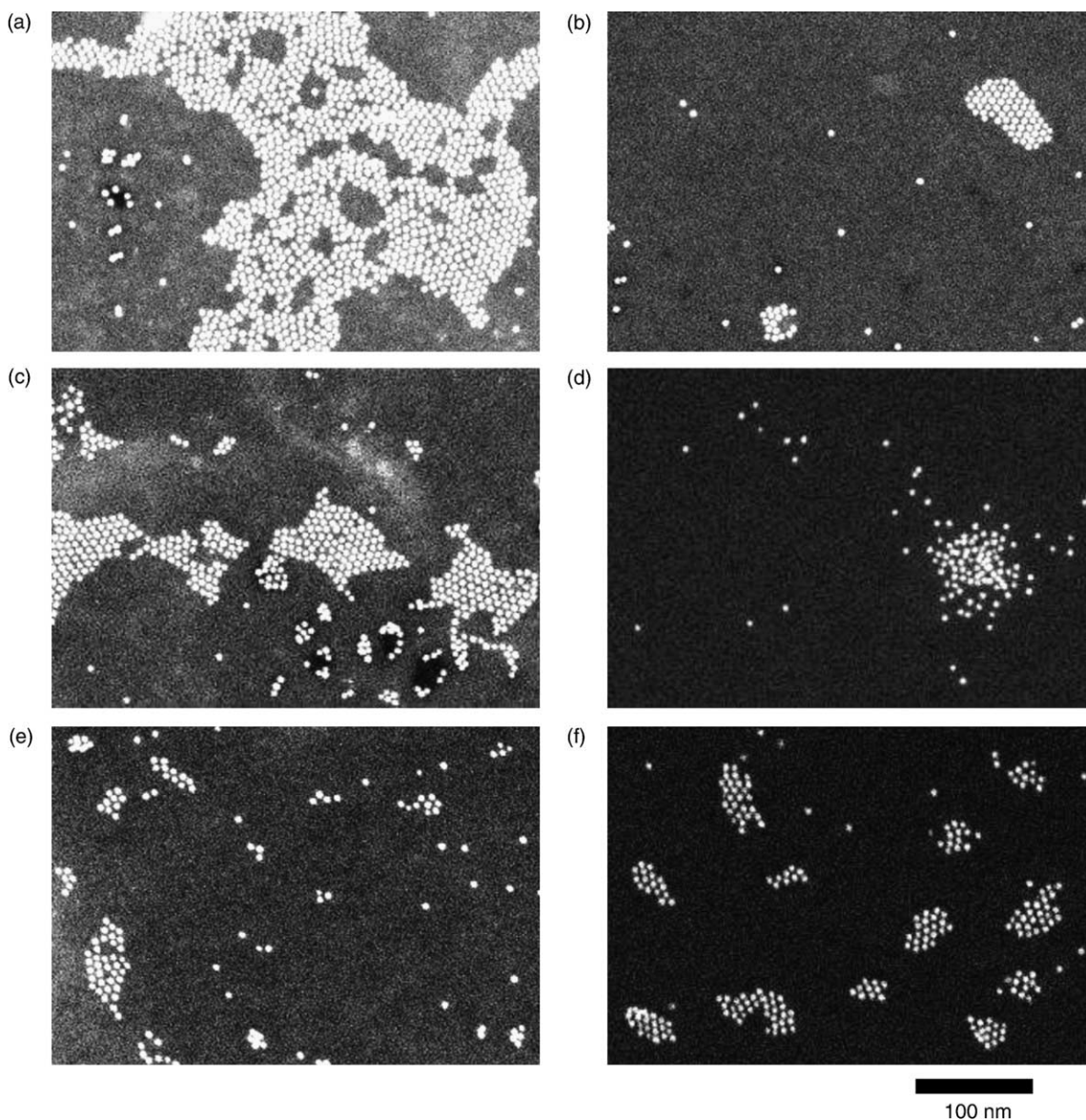


Fig. 4. TEM images of representative samples: (a) PS high-loading film; (b) PS low-loading film; (c) MEH-PPV high-loading film; (d) MEH-PPV low-loading film; (e) PMMA low-loading film; (f) PF low-loading film.

4. Conclusions

We demonstrate high photoluminescence quantum efficiency in the near-infrared range for NCs embedded in polymers. We built a setup, involving an integrating sphere, that measures the absolute PLQE of the NCs in films without the need for reference dyes. Transmission electron microscopy was used to establish a correlation between film morphology and PLQE: the smaller the NC domains, the higher the PLQE of the NCs. In the best case, the PLQE of the NCs in a polymer film reaches 12% which is at least an eight-fold increase from those of pure NC films emitting in the NIR range reported previously. As this property was found for polymer matrices which are semiconducting, the films we made could be used directly as the luminescing layer of an electrolumi-

nescent device. These findings provide insight into device design towards increasing the efficiency of NC-based LEDs.

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